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6. AUTHOR(S)
Dr. Alan R. Katritzky

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)
Center for Heterocyclic COmpounds
Department of Chemistry
University of Florida
Gainesville, FL 32611-7200

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13. ABSTRACT *(Maximum 200 words)*

Final Progress Report includes a brief summary of research findings made during the work on the project. The main purpose of the project was to synthesize and characterize organic compounds as potential surface coatings for SAW and chemical microsensors.

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"DETECTION AND IDENTIFICATION OF AIRBORNE CONTAMINANTS"

FINAL TECHNICAL REPORT

ALAN R. KATRITZKY, P.I.

06.10.96

U.S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAL03-92-G-0195

CENTER FOR HETEROCYCLIC COMPOUNDS,
UNIVERSITY OF FLORIDA

Statement of the Problem Studied

The research under the titled Project was focused on the synthesis of organic heterocyclic compounds as a potential SAW (surface acoustic wave) and chemiresistor coatings towards vapor challenges of airborne contaminants.

Summary of the Most Important Results

During the first year of the Project the study of the surface modifications of the Polyamidoamine (PAMAM) Starburst Dendrimers and some other similar systems was performed. Based on the current collaboration between Dr. D. Tomalia research group (Michigan Molecular Institute) and CRDEC on the study of such polymers, we attempted the chemical surface modification of the PAMAM Dendrimers. Polymers with generations G = 1.0, 1.5, 2.0, and 2.5 were studied (specimens of these PAMAM were received from Dr. Tomalia). PAMAM Dendrimers exist as full generations (terminal amino groups, G = 1.0, 2.0, etc.) or as half generations (terminal ester groups, G = 1.5, 2.5, etc.). Generations 1.0 and 2.0 undergone the Mannich reaction with formaldehyde and benzotriazole to form the aminals in good yields. ^{13}C NMR quantitative spectra have indicated complete conversion of the terminal amino hydrogens for both generations. The half generations (G = 1.5 and G = 2.5) have been treated with N-(2-aminoethyl)pyrrole. However, no reaction has been observed even after two weeks. Consultations with the research group of Dr. Tomalia revealed that in some chemical reactions the behavior of PAMAM Dendrimers is unpredictable and highly depend on the specific reaction conditions. Besides that, isolation and characterization of the reaction products proved to be problematic because of the large size and polymeric nature of their molecules. Therefore, we switched our further experiments to another model, tris-(2-aminoethyl)amine (TRIS). It has the branching pattern G = 0 without the

presence of amido group, allowing more freedom for reaction conditions and purification methods.

During the second year of the Project, we elaborated several reactions for the TRIS terminal amino group modifications. Specifically, we have prepared and characterized 2,5-dimethyl-1-pyrrolyl- and (1-benzyl)-4-piperidin-4-yl derivatives of TRIS; its amino groups were also converted into trimethylammonium chloride salt and several pyridinium salts. All the derivatives of TRIS were obtained in good yields and with practically quantitative conversion of the terminal amino groups, which gives a good chance for the reactions employed to be transferred on the surface modifications of PAMAM Dendrimers.

Then we turned our attention to 1,3,5-triphenylformazans and two related classes of nitrogen-containing heterocycles, 2H-tetrazolium salts and verdazyls (highly stable free radicals). These compounds possess structures close to those of phthalocyanine dyes, which showed good results as coatings for chemical microsensors. Formazans, tetrazolium salts and verdazyls form complexes with metals, possess redox properties and have some other specific features which support their potential as microsensor coatings. We developed new and effective method for the oxidative ring closure of 1,3,5-triarylformazans by means of reaction with mild oxidating agent, 1-chlorobenzotriazole, which afforded the corresponding 2,3,5-triaryl-2H-tetrazolium chlorides [94H73]. A series of previously prepared 1,3,5-triarylformazans containing both electron-donating and electron-withdrawing substituents was thus converted into tetrazolium salts in high yields. In the verdazyl series, we elaborated the new method for the preparation of verdazyl radicals containing various substituents at the C(3)-position of heteroring. Employing phase-transfer catalysis (solid-liquid phase transfer) in the presence of crown-ether (DC18C6), we were able to prepare a series of verdazyls with middle- and long-

chained aliphatic substituents at the C(3) position. Moreover, this method was extremely useful for the preparation of the 3-[N,N-di(cyclo)alkylamino]substituted verdazyls - almost unknown until now class of verdazyl radicals. We synthesized eight new radicals of such type, of which the first N,N'-linked at the C(3)/C(3') positions bis-verdazyl [94CJC1849].

Third year of the Project we devoted to the study of the synthesis of formazans under phase-transfer conditions. Formazans are well-known compounds in the dyes industry. However, previously known methods for their preparation are suffering from several drawbacks, of which the necessity to use low temperatures and toxic (pyridin) solvents is most limitng. We developed a new synthetic pathway to prepare 3-(substituted)-1,5-diphenylformazans, which involves the promotion of azo-coupling of aryldiazonium salts with aldehyde arylhydrazones by phase-transfer catalysts (onium salts and crown ether, DC18C6) [94S577]. The reaction is carried out under mild basic conditions in liquid-liquid two-phase medium at elevated temperatures. Based on this new method, we also developed the one-pot procedure for the preparation of variously substituted 1,3,5-triarylformazans without isolation of the intermediate arylaldehyde arylhydrazones, which have been required by traditional methods. A double azo-coupling reaction of phenyldiazonium chloride with several different CH-active compounds afforded the corresponding formazans only in the case of phenylpyruvic acid or malonamide, but for these cases it was highly efficient.

One of the Project goals was to design new molecules-ligands for metal cations. Complexes of organic ligands with metal cations proved to have great potential as chemical microsensor coatings. We employed the new phase-transfer catalyzed methodology (see above) for the construction of the first lariat crown-formazan, prototype of a new series of podandocoronands. As previously shown, podandocoronands are some of the strongest known ligands of metal cations,

providing a three-dimensional cation binding. We prepared a macrocyclic formazan with pendant functionality which was then modified into a macrocycle with a side arm carrying a strongly electron-donating (dimethylamino) group [94TL6465]. Development of this topological approach, combined with synthetic possibilities in the formazan series (see above), offers much potential for the preparation of a wide variety of useful lariat crown-formazans, extremely interesting potential microsensor coatings.

The research during the last year of the Project was concentrated on further dvelopment of lariat crown-formazan concept. Thus, we converted the macrocyclic formazan with pendant functionality into the corresponding stable free verdazyl radical (four-step synthesis) containing a readily modified pendant hydroxy group. ESR investigations revealed that this new macrocyclic verdazyl radical has unique paramagnetic properties reflected in unusual spectral characteristics compared to the other verdazyl radicals. The presence of pendant functionality opens the possibility of free radical chemical modification in so-called "free-spin-conservation" manner, where the unpaired electron does not participate in the reaction (most unusual chemical behaviour). This potential modification of macrocyclic verdazyl radicals might be used in order to expand the family of chemical microsensor coatings.

We also elaborated the new method for the preparation of related to verdazyls class of organic dyes, i.e., verdazylium salts. 6-(4-Substituted-phenyl)-2,4-diphenylverdazylium salts were prepared by the reactions of 3-(4-substituted-phenyl)-1,5-diphenylformazans with formaldehyde and different organic and inorganic acids in a two-phase chloroform-water medium by brief and gentle heating. It appears that self-phase-transfer catalysis is involved in the course of reaction, a behavior which is most uncommon among organic reactions. Subsequent reductions of the verdazylium salts thus prepared with excess ascorbic acid in the two-phase system give the corresponding verdazyl radicals, while in methanol the reduction proceeds to form

leuco-verdazyls [96S000]. This finding adds a valuable extention to the known methods for the preparation of verdazyls, leuco-verdazyls, and verdazylium salts.

In addition, we continued the investigations in the preparation of organic ligands from formazan series. Thus, we explored a new pathway for the synthesis of podands containing formazan moieties at the end of oligoethyleneglycol chain. We developed a simple and effective method for the preparation of hydroxyphenyl-substituted formazans which were previously difficult-to-access, and prepared several bis-formazans containing the oligoethyleneglycol bridge of various length between two formazan units. This new series of bis-formazans would be able to trap the metal cations of different sizes depending on the length of the bridge, thus enhancing the potential of such formazans as chemical microsensors. A manuscript incorporating this synthetic results is now on the stage of preparation.

In summary, over 70 new organic compounds, potential coatings for SAW and chemical microsensors, were prepared under subject agreement. Unfortunately, it was not possible to perform the initially scheduled testing of these new potential coating materials here at our facilities. Preliminary results were obtained on the testing rig having a lower frequency, however this was found to be insufficiently sensitive for the testing of the new series. Procurement of a new rig would have required substantial additional financing and human resources, therefore, during the joint meeting with CRDEC representative, Dr. H. Dupont Durst (meeting held on March 4, 1993), it was decided to concentrate the efforts on the synthesis of the new potential coatings with possible further transfer of results and materials to CRDEC, to perform testing using its own facilities.

List of All Publications and Technical Reports Published

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96S000 A. R. Katritzky, S. A. Belyakov. A direct one-step preparation of triarylverdazylium salts from corresponding triarylformazans. *Synthesis*, 1996, *submitted*.

List of All Participating Scientific Personnel Showing Any Advanced Degrees Earned By Them While Employed on the Project

Dr. J. N. Lam

Dr. Maria Szajda

Mr. D. Cheng

Dr. S. A. Belyakov

Dr. T. Mayelvaganan

Report of Inventions - None.

Bibliography - see above, "List of All Publications and Technical Reports Published".